

## Target effective emission coefficients during reactive sputtering of oxides and nitrides

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### Abstract

In the field of magnetron sputtering, reactive sputtering is becoming more and more important as it allows to widen the scope of materials that can be deposited. Not only high quality metal coatings can be deposited, but also a wide variety of compounds such as oxides and nitrides can be obtained by adding a reaction gas, for instance oxygen or nitrogen to the sputtering gas. By doing this, compounds are not only deposited on the substrate, and inner walls of the equipment but also on the cathode or target. On the target surface the growth of this compound layer is the result of the competition between shallow implantation of reaction gas ions, chemisorption and knock-on implantation and the sputter etching of the surface by essentially sputter gas ions. This effect of target coverage is called poisoning and affects the deposition speed, discharge stability and cathode or discharge voltage. The discharge voltage is a very sensitive parameter for controlling the composition of the growing compound layers on the target. The understanding of its behaviour is important for controlling the reactive sputter process. This discharge voltage, which is an easily accessible quantity, is closely related to a more fundamental quantity, i.e. the ion induced secondary electron emission coefficient or  $\eta_i$  and gives the average number of electrons ejected out of a particular material upon impact by an ion.

Based on the well known Thornton relation, which shows that the discharge voltage is inversely proportional with the  $\eta_i$  value, a measuring procedure was developed that allows to measure an effective  $\eta_i$  for compound materials as they cover the sputter cathode with a layer of about 2 nm thickness during reactive sputtering.

In this study, the effect of oxidation and nitridation of the target on the  $\eta_i$  value is studied. In general, the emission coefficient of these compounds depends on their electronic properties. Indeed, “wide gap” nitrides such as AlN and Mg<sub>2</sub>N<sub>3</sub> have a high emission coefficient, while “narrow gap” and nitridic conductors display a low coefficient of emission. The same seems to hold for oxides. Oxidic insulators as MgO, Al<sub>2</sub>O<sub>3</sub>, ..., also “wide gap” materials, are also characterised by high  $\eta_i$  values or emission coefficients. However, for oxides, the behaviour is complicated by a possible reduction and growth of sub oxides under ion bombardment. Regarding emission coefficients, a clear distinction should be made between oxides that sputter congruently without any surface reduction upon ion impact and oxides that are reduced under impact of sputter gas ions. The former oxides which keep their bulk electronic properties down to the surface under ion impact, are also characterised as “wide gap” materials yielding high emission coefficients. On the contrary, oxides subjected to reduction under ion bombardment are characterised by  $\eta_i$ -values slightly smaller than those of the parent metal.

### 1. Introduction

From a technological point of view, magnetron sputtering is a well established technique and has wide spread applications in the field of coatings. In particular, reactive sputtering has widened that scope considerably as it allows to deposit a broad variety of compound coatings such as oxides, nitrides, carbides, etc. However, this broadening has a price, namely an instability in the sputtering behaviour called poisoning. Due to that poisoning not only an

instability and a hysteresis effect is created but in general, the deposition speed is also reduced considerably.

Despite the fact that the origins of the poisoning effect are understood quite well [Depla 2007], [Berg 2005] some problems remain. When a hysteresis experiment is performed, the deposition speed and the discharge or target voltage are monitored as a function of the amount of reaction gas added to the sputter gas which is mostly argon. If pumping speeds are not too high, there is a particular amount of reaction gas which makes the system unstable and drives it into poisoning or poisoning mode. Lowering the partial pressure of the reaction gas brings the system back into the original situation in which essentially metal is sputtered (metal mode) and nearly no compound. This return to metal mode sputtering shows a hysteresis behaviour in other words, the process path followed upon increase of the flow of reaction gas is different as compared to the path followed upon decrease and if no specific measures are taken, the system switches abruptly between metal mode and poisoning mode. The system can be stabilized by using either optical spectroscopy or by mass spectroscopic means which increases and the cost of investment and the complexity of the equipment. The main origin of the poisoning instability is the growth of the compound not only on the substrate and inner walls of the equipment, but also on the target which changes completely the magnetron discharge and gives often rise to a reduction in deposition speed and an increase in arcing behaviour as those compounds are frequently bad electrical conductors. Stoichiometric compounds are mostly obtained just before the sputter process goes into full poisoning mode. On the other hand, as deposition speeds for the compounds, should also be kept as high as possible, one is tempted to use the system close to metal mode, in other words, the regime of choice is exactly that unstable regime! As already mentioned, not only the deposition speed suffers by the poisoning process, but also the target voltage shows a similar instability. Measuring the target voltage is a simple and straightforward means of monitoring the reactive sputter process and the associated instabilities. However, upon poisoning, the deposition speed is normally reduced, but the behaviour of the discharge voltage is unpredictable. Typical examples are the reactive sputtering of Al in a mixture of argon and oxygen in which the target voltage decreases upon poisoning and the reactive sputtering of Ti in a similar gas mixture where poisoning is manifested as an increase in target voltage. This behaviour is clearly dependent on the target material but unpredictable and a fortiori not understood. This lack of understanding has been a continuous source of frustration in the “sputtering” community and is the subject of this contribution.

## **2. Experimental**

The experimental set up has been fully described in literature [Depla 2006]. In a typical poisoning experiment in which the discharge voltage is monitored as a function of the ratio of partial pressures or flows of reaction gas and sputter gas, the interpretation of the target voltage is not straightforward. Indeed, variation of that ratio or plasma composition has not only an influence on the target condition, but also on the plasma condition. In other words, by varying the amount of reaction gas, not only the target impedance is changed but also the plasma impedance and due to the complex interplay between plasma and target it is impossible to retrieve information on the target condition alone.

Therefore a measuring scheme was developed in which the plasma conditions remain unchanged and variations in target voltage can be attributed solely to a variation in target condition. First, the metal target was sputter cleaned in pure argon until the target voltage was fully stabilized after which the magnetron discharge was stopped and the sputter gas was evacuated. Then the system was backfilled with pure reaction gas (oxygen or nitrogen) and the magnetron was again started. This manipulation took a couple of seconds. Again the discharge voltage was monitored until it stabilized, this voltage was measured as  $V_{RG}$  ( $RG =$

N<sub>2</sub> or O<sub>2</sub>) and the discharge was stopped. After pump down of the system, removing all reaction gas, pure argon was reintroduced and the discharge restarted.

The next step of the measuring procedure was the registration of the discharge voltage as a function of time when the discharge was switched on in pure argon to follow the return of the discharge voltage to its value measured in pure argon. This voltage was measured (with a sampling rate of 1 kHz) as  $V_{Ar}$  and corresponds to metal mode sputtering. When the DC voltage generator is switched on, a constant output voltage can be obtained within its ramp time of 30 ms as mentioned in the manual and as experimentally verified. According to the literature it has been proven by optical emission spectroscopy during pulsed magnetron sputtering that within 40  $\mu$ s a stable discharge voltage is obtained. Hence, the discharge voltage registered 30 ms after switching on the power supply depends solely on the condition of the target due to plasma oxidation/nitridation and not on transients in the output voltage in the start-up of the power supply (this discharge voltage was noted as  $V_{C,Ar}$  with C = Nitr. or Oxid and corresponds to deep poisoning). Moreover, as one goes through the whole etching cycle from a fully oxidized or nitrided target back to a pure metallic target while keeping the plasma conditions constant (with respect to pressure and sputter gas), the observed variations in discharge voltage are only related to variations in target conditions. This in contrast with hysteresis experiments where the target condition is changed by continuously adding reactive gas to the sputter gas and thus varying the plasma condition together with the target conditions.

### 3. The Thornton relation

In his paper “Magnetron sputtering : basic physics and application to cylindrical magnetrons”, J.A. Thornton [Thornton1978] derives a zero-dimensional formula for the discharge voltage based on energy conservation arguments, i.e. the energy input into the discharge has to be equal to the energy consumed by the discharge for excitations and ionizations. The discharge sustaining mechanism is generally based on the emission of secondary electrons from the cathode by ion bombardment, and the emitted electrons gain energy by acceleration over the dark space. These electrons will have a minimal energy  $eV_{min}$  with  $V_{min}$  the minimal discharge voltage to sustain the discharge. For the production of the necessary ions, an energy of  $W$  is needed, with  $W$  the effective ionization energy which is in the order of 30 eV for magnetron argon discharges. Hence, the number of formed electrons is equal to  $eV_{min}/W$  if no electrons are lost. To account for electron loss, Thornton introduces  $\epsilon_e$  which is the fraction of the full complement of ions  $eV_{min}/W$  that is made by the average emitted secondary electron before it is lost from the system. The formed ions will bombard the cathode, and secondary electrons are emitted. Of course, one should take into account that some ions will not reach the cathode, and therefore the ion collection efficiency  $\epsilon_i$  is introduced. If  $\gamma_{eff}$  is the effective number of emitted electrons,  $\gamma_{eff} \epsilon_i \epsilon_e eV_{min}/W$  electrons are emitted from the cathode. To sustain the discharge, this number should be at least equal to 1, resulting in the Thornton equation for the minimal discharge voltage,

$$V_{min} = \frac{W}{\epsilon_e \epsilon_i \gamma_{eff}} \quad (1)$$

The effective Secondary Electron Emission Yield,  $\gamma_{eff}$  depends on the discharge conditions as shown by Buyle et al. [Buyle2005].

In magnetron sputtering,  $\epsilon_o$  and  $\epsilon_i$  are approximately equal one. It was shown by [Buyle 2005] that the effective emission coefficient  $\epsilon_{eff}$  is related to the intrinsic emission coefficient  $\epsilon_i$  by

$$\epsilon_{eff} = m.f.\epsilon_i \quad (2)$$

with  $f$ : effective gas interaction probability

m: a multiplication factor

The effective gas interaction probability  $f$  takes into account possible effects of electron recapture with the target. As already indicated by Thornton, electron recapture at the cathode can play an important role. Indeed, due to the low magnetron discharge pressure a large fraction of the emitted electrons can reach the cathode without gas interaction, and therefore without energy loss. This means that they can turn back to the cathode with their original energy on emission, resulting in a possible recapture. The probability of the possible recapture is expressed as the reflection coefficient. This effect lowers the  $\eta_{\text{eff}}$ .

Taking equation (2) into account, a “revised” Thornton equation is obtained

$$V_{\text{min}} = \frac{W}{\epsilon_0 \epsilon_i (m.f) \gamma_i} \quad (3)$$

It can be shown that the product  $(mf)$  is fairly constant under the given experimental conditions and for the different target materials under consideration, metals and their oxides and nitrides. With those assumptions it is seen that the inverse of the target voltage is proportional to the electron emission coefficient  $\eta_i$ .

In Fig. 1 one sees this relationship for 4 sets of experimental conditions of discharge current and argon sputter gas pressure. In this figure, the experimentally obtained values of the inverse of the discharge voltages of 18 different metals are plotted versus their mean value of the emission coefficient  $\eta_i$ . Values of  $\eta_i$  of each metal were obtained from literature and from theoretical calculations (see next paragraph eq. 4). From these values, a mean value of  $\eta_i$  was calculated corresponding with the position of the markers in Fig. 1 and the width of the given interval corresponds with minimum and maximum values of  $\eta_i$ . As can be seen, there is indeed a linear relationship between the inverse of the target voltage and the  $\eta_i$  values for each set of experimental parameters and the slope of this fitting line depends on these experimental conditions. The fact that a linear relationship is observed gives credit to the assumption made that the product  $f.m$  is constant in the parameter range under consideration. Conversely, this linear fit can in turn be used to extract the emission yield  $\eta_i$  from the measured discharge voltage as long as the same experimental conditions are maintained.

#### 4. The ion induced secondary electron emission coefficient $\eta_i$

As can be seen from eq. 3, and when comparing the discharge voltage of different materials the value of  $\eta_i$  is the important factor as it is the only real material dependent quality in that equation. Hence, at least a few words should be spent on this topic. Two excitation mechanisms are generally discussed for electron emission by ion impact : potential emission and kinetic emission. For kinetic emission, the kinetic energy of the ion is used to emit electrons. The electrons are excited due to the Coulomb interactions between the impacting particle and the surface. The excitation of “nearly free electrons” of metals by light ions is the dominant mechanism for kinetic electron emission for these materials. For heavier ions, another excitation mechanism is important. This is the so-called electron promotion mechanism where electrons are emitted into vacuum via electron promotion of transient molecular projectile-target orbitals.

Also, the potential energy can be used to emit electrons. This mechanism, potential emission, is important at low kinetic energy of the ion, and is the major mechanism for electron emission from metal surfaces. The electron excitation occurs through a two-electron Auger process. This can be a so-called Auger neutralization of the ion, i.e. the electron is captured by the ion, and a second electron is excited. Another possibility is the Auger deexcitation mechanism where the electron is captured by the ion and the excited projectile releases an electron to relax to a lower energy state. Electron emission from a metal is only possible when the ionisation energy of the ion  $E_i$  exceeds twice the work function  $\phi$ . Also, this means that

the maximum kinetic energy of the emitted electrons is  $E_i - 2\phi$ . This explains in some way that published empirical formulas for  $\gamma_i$  for metals are related to this latter quantity, i.e.

$$\begin{aligned} \gamma &= 0.032(0.78E_i - 2\phi) && \text{[Baragiola1979]} \\ \gamma &= 0.016(E_i - 2\phi) && \text{[Raizer1991]} \\ \gamma &= 0.2(0.8E_i - 2\phi)/E_F && \text{[Kishinevsky1973]} \end{aligned} \tag{4}$$

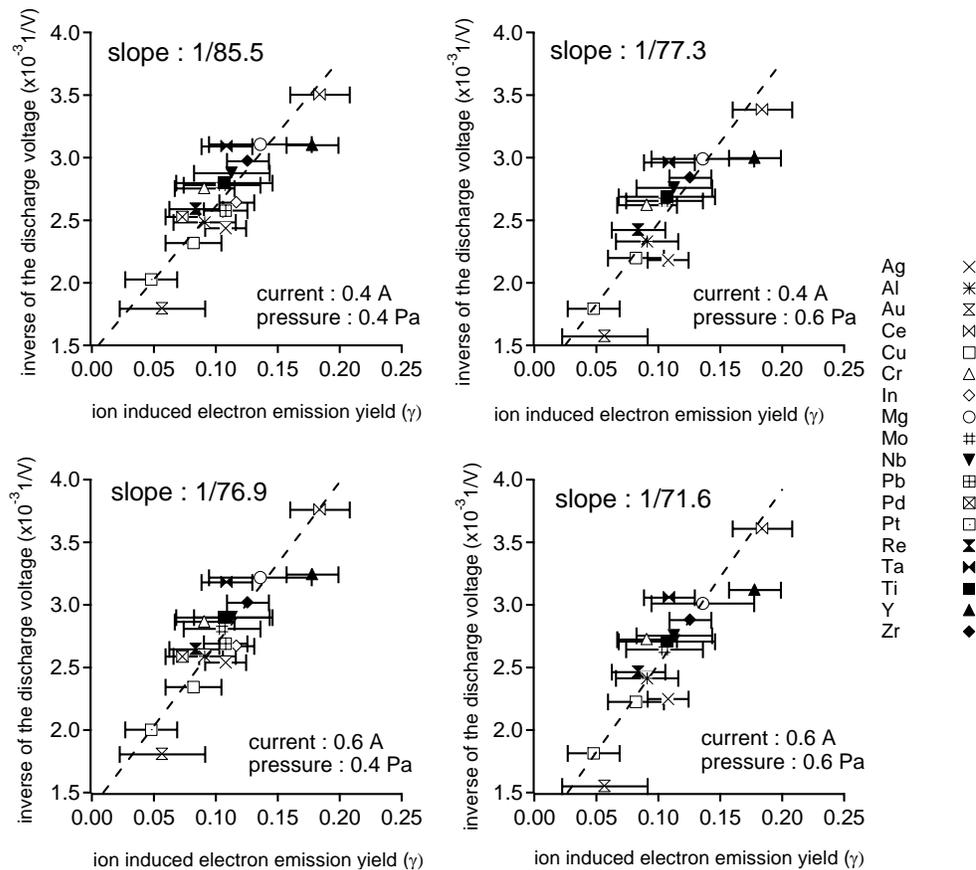


Figure 1. The inverse of the discharge voltage as a function of  $\gamma_i$  for different target materials under several experimental conditions. The measurements were performed with a conventional two inch magnetron in a pure argon atmosphere. All targets had a purity of 99.99%. The dotted line is a linear fit. For all conditions the correlation coefficient has a value in the interval 0.87-0.89.

In summary, one can say that potential emission is the mechanism of choice for the electron emission at metal surfaces while kinetic emission is more typical for materials such as oxides. The latter is also characterized by a much higher yield  $\gamma_i$  as compared to the yield of metal surfaces explaining for instance the use of MgO as an emitter in plasma displays.

## 5. Nitride experiments

As outlined in section 2, prior to each experiment, the target was sputter cleaned in pure argon. In a first series of experiments, each metal target was exposed to a pure nitrogen plasma until a stable discharge voltage was registered, discussed further in the text as  $V_{N_2}$ . After plasma nitridation, the target was sputter cleaned in pure argon until a stable discharge

voltage was again registered, referred to as  $V_{Ar}$ . Each experiment was repeated under different conditions of magnetic field strength, discharge current and gas pressure. In total five series of experiments were performed. The first voltage registered 30 ms after discharge ignition in pure argon is  $V_{nitr,Ar}$ , or the discharge voltage of a nitrated target measured during sputtering in pure Ar. Figure 2 compares these three different discharge voltages, measured under the same conditions for different materials.

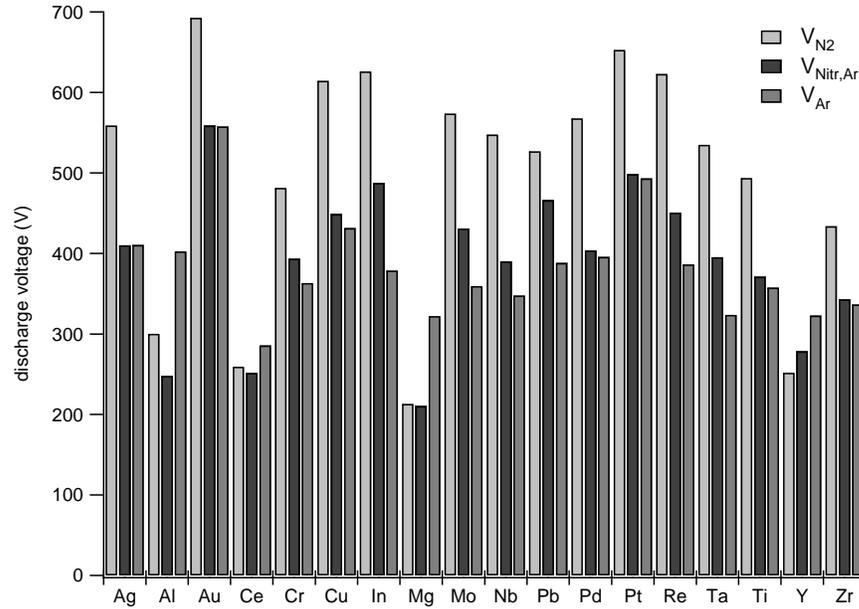


Figure 2. Comparison between the discharge voltage measured in pure Ar ( $V_{Ar}$ ), pure nitrogen ( $V_{N_2}$ ) and the discharge voltage of an nitrated target in pure Ar ( $V_{nitr,Ar}$ ).

From Fig. 2, it follows that for most materials the discharge voltage in argon of the nitrated target,  $V_{nitr,Ar}$  is higher than the discharge voltage measured under the same conditions for the metal target ( $V_{Ar}$ ). This effect can only be explained by the change of the ion induced  $\phi_i$ . Based on the reasoning given in paragraph 3 this high voltage is related to a low  $\phi_i$ , which is an interesting result with respect to the understanding of the emission mechanisms for this class of materials. To facilitate the discussion one can use the results shown in figure 1 to calculate the  $\phi_i$ . Indeed, as the discharge voltage of the nitrated target surfaces is measured under identical conditions as for the metals, the fitted line (see figure 1) can be used as a calibration line which relates the measured discharge voltage to the  $\phi_i$ . Of course, as shown in figure 3, the material dependency shown in figure 2 is reflected in the calculated  $\phi_i$ , i.e. for one group of materials (Ce, Al, Mg and Y) the  $\phi_i$  increases as compared to the metal while for the other metals the nitrated target has a slightly lower  $\phi_i$ . For the most noble materials the effect of nitridation is negligible as can be understood from the low negative or positive formation enthalpy.

For nitrides hardly any information can be found on the ion induced  $\phi_i$  values. For oxides more data on the  $\phi_i$  can be found. For this latter class of materials (see also further) a higher  $\phi_i$  than the metal is generally reported which is related to the electronic properties of these materials. In this context it is interesting to notice that metal nitrides are categorized in two groups. In the first group metal-nitrogen (M-N) interactions are dominant. With this type of bonding, it is not surprising that the physical properties of these ionic/covalent metal nitride compounds are very different from the associated metal. In the second category are the metal

nitrides with dominant metal–metal (M–M) interactions, such as the Group IVB–VIB transition metal nitrides. One peculiarity of this kind of metal nitrides is that their electrical conductivities are similar to those of the parent metals, and as a consequence, are often considered as conductive ceramics. The difference between these two groups of nitrides is of course also noticed in the band gap of these materials. AlN (band gap 6.2 eV [Saib2006]) and Mg<sub>2</sub>N<sub>3</sub> (band gap 2.8 eV [Fang1999]) are wide band gap materials. As figure 9 shows, these two nitrides have a high  $\gamma_i$ . A small increase of the  $\gamma_i$  is noticed for CeN (band gap 1.76 eV [Xiao1998]) and YN (band gap 1 ~ 2 eV [Takeuchi2002]), two materials with an intermediate band gap. The other nitrides are semiconductors with a minor band gap (CrN: 0.071 eV [Constantin2005], Cu<sub>3</sub>N: 0.23 eV [Hahn1996], InN 0.67 eV [Walukiewicz2006] or conductors (e.g. ReN[Soto2007], TaN, TiN, NbN [Kobayashi2001], ZrN[Jeng2007]). This latter group has a low value of  $\gamma_i$ . So, it seems that the  $\gamma_i$  of the nitrided targets can be directly related to their electronic properties.

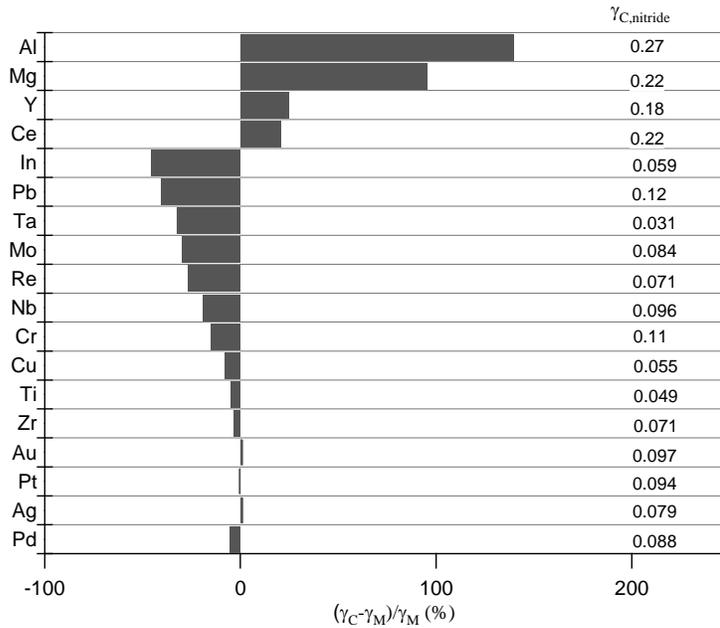


Figure 3. Relative change of the effective emission coefficient by nitridation of the metal target.  $\gamma_M$  and  $\gamma_C$  stands for respectively the  $\gamma_i$  of the metal and the compound.

## 6. Oxide experiments

Similar experiments as described in the previous paragraph have been performed with oxygen. Hence, all targets were plasma oxidized in pure oxygen, and the discharge voltage was registered during the target sputter cleaning in pure argon. Figure 4 shows the relative change of the effective emission coefficient by oxidation of the metal target.

As expected from the hysteresis experiments, two groups of metals are found, but this result is not so simple to explain from the electronic properties as for the nitrides. Most oxides shown in the list have a wide band gap and are excellent electrical insulating materials for which a high  $\gamma_i$  is expected. Moreover, a fit through a compilation of known data of  $\gamma_i$  for clean (metal) and dirty (oxidized) cathodes by Phelps et al. [Phelps1999](see figure 5) shows clearly that at sufficient high ion energy (above 250 eV)  $\gamma_i$  for oxidized surfaces is higher than for clean surfaces. In most cases  $V_{ox,Ar}$  for the oxidized surfaces is much higher than this threshold value and hence, one should expect a high  $\gamma_i$ , and consequently a low discharge voltage on oxidation as is the case for Al under poisoning.

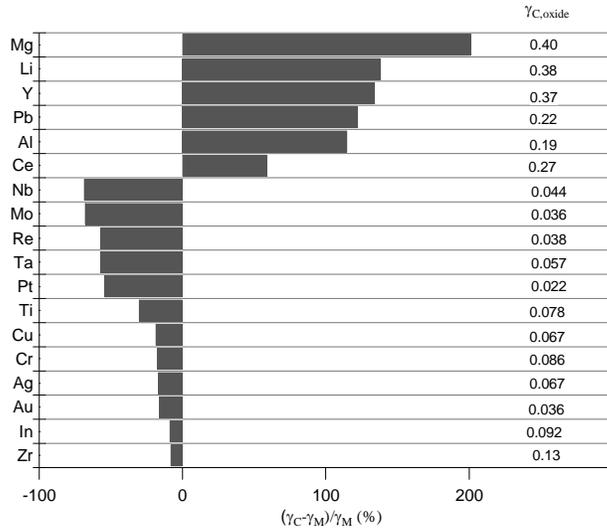


Figure 4. Relative change of the effective emission coefficient by oxidation of the metal target.

## 7. Discussion

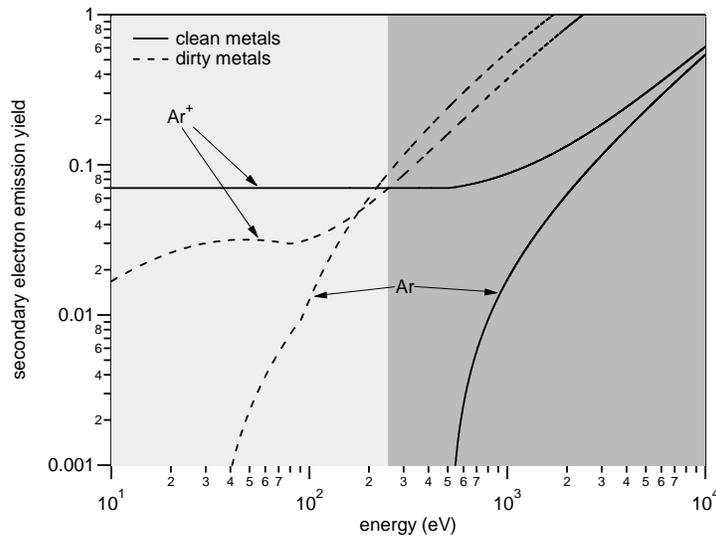


Figure 5.  $\eta_i$  for argons ion and fast argon atoms bombardment (after [Phelps1999]) of clean metals and dirty metals. Above 250 eV ions the  $\eta_i$  is substantially higher for dirty, oxidized surfaces as compared to the clean metal surface.

A possible explanation for the low  $\eta_i$  values for most oxidized surface is based on the work of Wittmaack [Wittmaack1999]. In this latter study, it is shown that the enhanced  $\eta_i$  generated by the oxygen implantation in silicon is directly proportional to the fractional coverage of the

surface with SiO<sub>2</sub>. Moreover, Wittmaack concludes that suboxides (SiO<sub>x</sub> with x<2) or isolated oxygen atoms embedded in Si, apparently produce only a negligible change in  $\Gamma_i$ . Wittmaack shows in the same study [Wittmaack1999] that bombardment of the formed silicon oxide layer by neon ions results in a rapid decrease of  $\Gamma_i$ . This effect is attributed to the preferential loss of oxygen during the neon bombardment. In conclusion it seems from this latter study that the  $\Gamma_i$  of suboxides is much smaller than for oxides and should be in the same order of magnitude of the  $\Gamma_i$  of the metal. In order to test Wittmaack's conclusion, five titanium suboxide targets were synthesized by sintering a mixture of Ti and TiO<sub>2</sub>. XRD measurements clearly show that both materials have reacted to a suboxide target. Based on XRD/RBS the stoichiometry of these suboxide targets was determined. By measuring the discharge voltage of suboxide targets under the same conditions as for the metal targets (see figure 6), the  $\Gamma_i$  of this type of materials can be obtained. After plasma oxidation in a pure oxygen plasma, approximately the same discharge voltage was registered for all targets, including a metal Ti target. Based on this result one can conclude that the target surface composition after plasma oxidation is equal for these materials. After sputter cleaning the target in pure argon, a discharge voltage dependent on the stoichiometry was registered. The discharge voltage for all suboxide targets was larger than the discharge voltage measured for Ti, indicating a lower value of  $\Gamma_i$  for these suboxide targets (see figure 6).

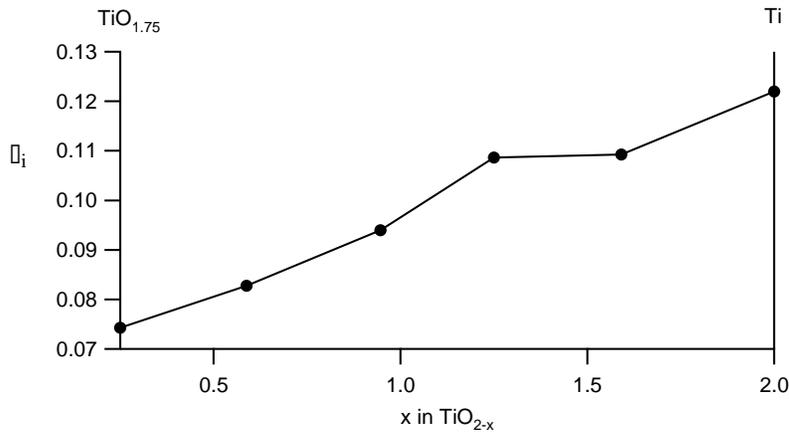


Figure 6. Calculated effective  $\Gamma_i$  as a function of the target stoichiometry for titania suboxide targets.

Hence, it seems that the statement by Wittmaack seems to hold, i.e. suboxide material has a lower  $\Gamma_i$  than the oxide. The low  $\Gamma_i$  of these titania suboxide targets is also consistent with the findings for the nitrides because the reduction results in a modification of the electronic structure of the oxide. Indeed, just the fact that these suboxides are electric conductive and that they can be sputtered in a DC process holds as a simple proof. So based on figure 6 one can conclude that the plasma oxidized targets with a low  $\Gamma_i$  are reduced, while the others are not. When studying the list of materials presented in figure 4, it is surprising to notice that the high  $\Gamma_i$  materials sputter congruently under ion bombardment, i.e. their stoichiometry and hence their electronic properties are not affected during ion bombardment. In other words, oxide materials, that sputter congruently are not subjected to preferential sputtering of oxygen and de facto do not suffer from reduction. Of the many studies on this topic of preferential sputtering of oxides, the work of Malherbe [Malherbe1986] has been chosen due to its simplicity to calculate a reduction factor, defined as

$$R = \frac{(X_M/X_O)^s}{(X_M/X_O)^b} \quad (5)$$

with  $X_i^s$  the surface fractional composition and  $X_i^b$  the bulk fraction composition. Based on the result of simple models for the preferential sputtering of binary alloys or compounds (such as oxides), Malherbe et al. proposed the following equation to relate the surface to the bulk composition,

$$\left(\frac{X_M}{X_O}\right)^s = \frac{Y_O}{Y_M} \left(\frac{X_M}{X_O}\right)^b \quad (6)$$

with  $Y_i$  the component sputter yield of the metal (M) and oxygen (O). From Sigmund's sputtering theory in the linear cascade regime, the ratio of the component sputter yields can be approximated by

$$\frac{Y_O}{Y_M} = \left(\frac{AM_M}{AM_O}\right)^{2q} \left(\frac{U_M}{U_O}\right)^{1-2q} \quad (7)$$

with AM the atomic mass and U the surface binding energy. The exact value of the parameter q is uncertain since q depends on the energy. For low ion energy a low value for q is generally accepted. As mentioned by Malherbe et al. the choice of the surface binding energies in equation (7) is "a notoriously difficult one due to the lack of reliable experimental data". Based on a modification of the Pauling formalism for bond energies, Malherbe et al. proposed a simple calculation scheme for the surface binding energy. Although, one can doubt this approach, and the calculated value of R is perhaps on its best a good approximation of the experimental reality, these calculations can give a reliable trend which shows the sensitivity of the oxide to reduce under ion bombardment. Based on published electronegativity values and bond energies, the value of R was calculated for all oxides using as bulk ratio the stoichiometry of the fully oxidized metal. The result of this calculation is given in figure 7.

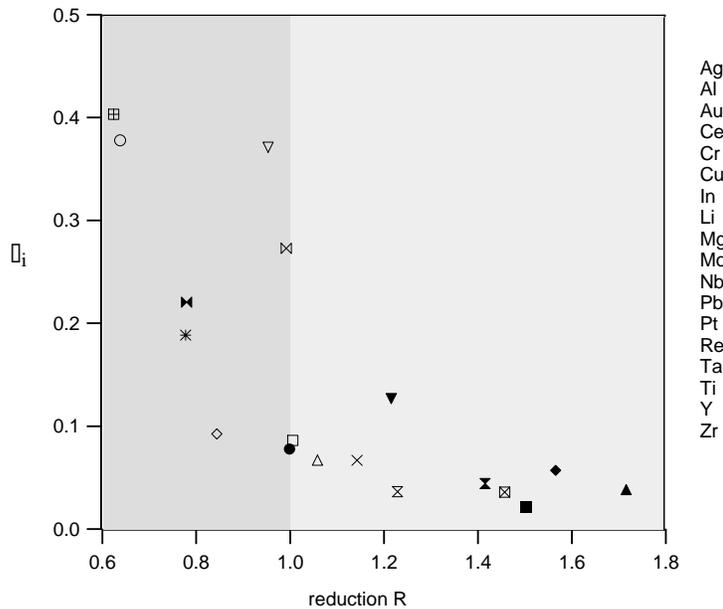


Figure 7. The calculated effective  $R_i$  for oxide as a function of the reduction factor (see equation 5) calculated with the model of Malherbe et al. (with  $q=0.05$ )

As figure 7 shows, the materials with a high effective  $R_i$ , or low discharge voltage during poisoned sputtering, have a low reduction factor, while the opposite is true for the materials with a low effective  $R_i$ . For In/O this reasoning does not hold as a higher value of R would be expected. Also, based on its  $R_i$  value one would expect a less strong reduction for Zr/O. From

the measurements with the titania targets and based on literature data (see compilation in [Malherbe1986]) a larger reduction of TiO<sub>2</sub> (in the order of 1.3) is expected.

Similar calculation for the nitrides shows no reduction, and therefore the  $\beta_i$  of the nitrides can be directly related to their properties. For oxides an increase of the  $\beta_i$  is expected but due to the formation of suboxides for some target materials this overall picture is more complicated but still consistent with the results of the nitrides. So, a clear distinction can be made between conducting materials (some nitrides, reduced oxides and metals) and materials with a wide band gap. The latter have generally a much higher  $\beta_i$  (see : the oxides of Al, Ce, Mg, Li, Pb and Y and the nitrides of Al, Mg, Ce and Y) than the originating metal. Although a complete analysis of the emission mechanism is needed to explain this difference, the idea behind these high  $\beta_i$  values is an emission mechanism different from potential emission which is typical for metals. For the metals, the work function defines the  $\beta_i$  under the assumption that the emission mechanism is only due to potential emission (see paragraph 4).

## 8. Conclusion

If it is assumed that the results obtained in this study for a wide range of nitrides, oxides and their parent metals can be generalized, the following conclusion can be drawn:

- Target poisoning in reactive magnetron sputtering and its influence on the discharge voltage largely depends on the behaviour of the Ion Induced Electron Emission Coefficients  $\beta_i$  of the compound (oxide, nitride...) formed on the target surface.
- The electronic properties of the very surface of the target define the  $\beta_i$  value of the target and the associated discharge voltage.
- Wide gap compounds have high  $\beta_i$  values as compared to the parent metal (Kinetic emission) and the discharge voltage decreases upon poisoning.
- Small gap, semiconducting and conducting compounds have low  $\beta_i$ -values. Whether or not these values are higher or lower compared to the parent metal will depend on electron densities and work function.
- This simple picture becomes blurred in magnetron sputtering as soon as preferential sputtering of the surface compounds occurs and this preferential sputtering alters the surface electronic properties. Many oxides are sensitive to preferential sputtering and are reduced under ion bombardment to suboxides which have a more metal like character as compared to the fully oxidized material. These suboxides will have a reduced  $\beta_i$  value and probably, the electron emission mechanism switches back from kinetic emission towards potential emission. This surface reduction will give rise to an "abnormal" increase in discharge voltage upon poisoning.
- The poisoning behaviour becomes predictable.

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